8-2004

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Hak-Jin Kim
University of Missouri

John W. Hummel
United States Department of Agriculture

Stuart J. Birrell
Iowa State University, sbirrell@iastate.edu

The Society for engineering in agricultural, food, and biological systems

The Canadian Society for Engineering in Agricultural, Food, and Biological Systems

Paper Number: 041044
An ASAE Meeting Presentation

Evaluation of Ion-Selective Membranes for Real-Time Soil Macronutrients Sensing

Hak-Jin Kim, Graduate Research Assistant

Biological Engineering Department, University of Missouri, Columbia, Missouri, USA, 65211, kimhj@missouri.edu

John W. Hummel, Agricultural Engineer

Cropping Systems & Water Quality Research Unit, USDA-ARS, Columbia, Missouri, USA, 65211, hummelj@missouri.edu

Stuart J. Birrell, Associate Professor

Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, Iowa, USA, 50011-3080, sbirrell@iastate.edu

Written for presentation at the
2004 ASAE/CSAE Annual International Meeting
Sponsored by ASAE
Ottawa, Ontario, Canada
1- 4 August 2004

Abstract. *On-the-go, real-time soil nutrient analysis would be useful in the site-specific management of soil fertility. The rapid response and low sample volume associated with ion-selective field effect transistors (ISFETs) make them good soil fertility sensor candidates. An important component of the ion-selective microelectrode technology is an ion-selective membrane that responds selectively to one analyte in the presence of other ions in a solution. This paper describes the evaluation of nitrate and potassium ion-selective membranes and the investigation of the interaction between the ion-selective membranes and soil extracting solutions to identify membranes and extracting solutions that are compatible for use with a real-time ISFET sensor to measure nitrate and potassium ions in soil. The responses of the nitrate membranes with tetradodecylammonium nitrate (TDDA) or methlytridodecylammonium chloride (MTDA) and potassium membranes with valinomycin were affected by both membrane type and soil extractant. A TDDA-based nitrate membrane would be capable of detecting low concentrations in soils to about 10^{-5} mole NO_3^-/L. The valinomycin-based potassium membranes prepared showed satisfactory selectivity performance in measuring potassium in the presence of interfering cations such as Na^+, Mg^{2+},Ca^{2+},Al^{3+}, and Li^+ as well as providing a consistent sensitivity when DI water, Kelowna, or Bray P_1 solutions were used as base solutions. The TDDA-based nitrate membrane and the valinomycin-based potassium membrane, used in conjunction with Kelowna extracting solution, would allow determination of nitrate and potassium levels, respectively, for site-specific control of fertilizer application.*

Keywords. *Ion Selective Electrode (ISE), Ion Selective Field Effect Transistor (ISFET), Ion-Selective Membrane, Sensitivity, Selectivity, Nitrate, Potassium, Soil extractant*

Introduction

Of the soil nutrients for plant growth, macronutrients including nitrogen (N), phosphorus (P), and potassium (K) are some of the most important components for crop production. Ionic forms of the macronutrients in the soil, such as NO_3^-, $H_2PO_4^-$, and K^+, are taken into plants through a combination of root interception, mass flow and diffusion processes.

Conventional soil testing methods to determine the amounts of macronutrients in soil have been generally carried out through a two-step process: soil sampling in the field and chemical analysis in the laboratory. The determination of the soil macronutrients is performed based on the pre-treatment of the soil sample involving drying and grinding, nutrient extraction processes by using soil extractants and filter papers, and the use of analytical instruments such as a cadmium reduction method for nitrate and the inductively coupled argon plasma (ICAP) spectrometry for phosphorus and potassium. These methods provide reliable results for the determination of plant-available nutrients in soil but require a lot of time and cost, thereby resulting in the limitation of number of samples to be analyzed for characterizing within-field variability in terms of soil nutrient. Time is a critical factor when sensing soil nitrate levels since the variability of soil nitrate levels may be quite high over time (Sudduth et al., 1997).

Ion-selective microelectrode technology, such as Ion Selective Electrodes (ISEs) and Ion Selective Field Effect Transistors (ISFETs), has been widely used in environmental monitoring and the biomedical field (Ammann, 1986). For example, solution pH measurement and blood-electrolyte determination are predominantly performed with ISEs and ISFETs.

The ion-selective electrode technology has been applied to the determination of soil nitrates in the laboratory using soil extracts by several researchers (Dahnke, 1971; Hansen et al., 1976; Li and Smith, 1984). They reported that the tested nitrate electrodes provided a rapid and convenient method of determining the amount of nitrate in the solution and were well suited for use in routine soil testing. Since the 1990's, more direct approaches to measuring nutrients in soil have been attempted with studies on the development of a real-time soil nutrient sensing system by several researchers (Adsett and Zoerb, 1991; Adsett et al, 1999; Adamchuck, 2002). The real-time system, which mainly consists of a soil sampler and a sensing unit, detects nutrients in the solution obtained from an extraction process or in a paste of soil and solution using commercial nitrate or potassium ion-selective electrodes. They reported that the ISE technology was adaptable to real-time soil nutrient sensing. However, inconsistent repeatability in sensor readings limited their use in practical systems.

The application of an ISFET chip combined with Flow Injection Analysis (FIA) has represented a great advance and has proven to be an interesting alternative to ISEs for the determination of soil nutrients since ISFETs have several advantages, such as small dimensions, low output impedance, high signal-to-noise ratio, fast response, and the ability to integrate several sensors onto a single electronic chip (Artigas et al., 2001; Birrell and Hummel, 2000). The results showed that the multi-ISFET sensor provided a good performance in predicting soil nitrates in manually extracted soil solution. However, a prototype automated soil extraction system (Birrell and Hummel, 2001) did not consistently provide soil extracts that could be analyzed by the ISFET/FIA due to blockages in the filtration process.

A key component of the ISEs and ISFETs is an ion-selective membrane that responds selectively to one analyte in the presence of other ions in a solution. The development of ion-selective membranes for various ions has progressed in recent years in the area of analytical chemistry. There are currently ion-selective membranes available for most of the important soil nutrients,

including NO_3^-, K^+, and Na^+ (Nielson and Hansen, 1976; Knoll et al., 1994, Tsukada et al., 1989; Artigas et al., 2001; Moody et al., 1988). Recently, several researchers have reported the development of a phosphate ion-selective membrane with acceptable sensitivity and good selectivity (Glazier and Arnold, 1988; 1991; Carey and Riggan, 1994; Liu et al., 1997).

To optimize yield and reduce excessive application of fertilizer, critical concentrations of each soil macronutrient must be established. This is a difficult task, because the critical concentration range of each macronutrient is usually influenced by many conditions such as crop type and time of soil sampling. However, according to a study on correlation of soil nitrate concentrations in late spring and corn yields in Iowa (Blackmer et al., 1989), 10 to 30 ppm NO_3 obtained from soil testing was considered as the critical range for optimum growth of corn. Haby et al (1990) reported that exchangeable soil potassium was well correlated with crop yields while showing an exponential curve with a critical range from 50 to 150 ppm K. Below the critical range, all the macronutrient needed to grow the crop needs to be applied as fertilizer; above the critical range, no additional fertilizer is needed.

In standard soil testing for the determination of soil macronutrients, various soil extracting solutions (soil extractants) containing certain cations and anions are used for extracting nutrients from soil through the shaking and filtering processes. For example, distilled water, 2M KCl, and 0.01M $CuSO_4$ solutions are used for nitrate extraction (Dahnke, 1971; Van Lierop, 1986; Yu and Ji,1993) and in the Mid-West area, available soil potassium and phosphorus levels are usually determined with 1M NH_4OAc and Bray P_1 (0.025M HCl + 0.03M NH_4F) solutions (Missouri Agricultural Experimental Station, 1998), respectively. However, due to the differences in the distribution of potassium and phosphorus among acidic and calcareous soils, several other soil extractants such as Olsen and Morgan solutions are used in soil testing laboratories in the USA (Haby et al., 1990).

The development of a real-time soil macronutrient sensor requires the use of a universal extracting solution that simultaneously extracts plant available levels of nitrate, phosphorus, and potassium from soils and reduces the amount of soil preparation required for detecting different nutrients. The Mehlich III extractant (0.2M CH_3COOH + 0.015M NH_4F +0.25M NH_4NO_3+ 0.013M HNO_3 + 0.001M EDTA) was proposed as a universal extractant to allow soil testing laboratories to use one extractant to simultaneously extract both phosphorus and cations contained in soil (Mehlich, 1984; Fixen and Grove, 1990). Van Lierop (1986; 1988; 1989) reported that the Kelowna multiple ion extractant (0.25M CH_3COOH + 0.015M NH_4F) could be used when determining soil nitrate concentrations, as well as when extracting phosphorus and potassium.

The aim of our research is the development of a real-time soil nutrient sensor using ion-selective membranes for the simultaneous determination of nitrate, phosphorus, and potassium levels in soil. In this paper, we describe the sensing characteristics of nitrate and potassium ion selective membranes tested in different soil extractants.

Objectives

The overall objective of this research was to investigate the suitability of different ion-selective membranes for sensing important soil macronutrients such as NO_3^-, $H_2PO_4^-$, and K^+ in order to develop a multi-ISFET chip integrated with an automatic soil extraction system for real-time soil analysis. As a first step to achieve this goal, various nitrate-selective membranes using a PVC polymer matrix technique were prepared and evaluated in different base solutions (Kim et al.,

2003). This paper describes the evaluation of potassium-selective membranes for soil potassium sensing and the investigation of the interaction between potassium-selective membranes and standard soil extractants, as well as summarizing updated results on the nitrate-selective membranes. Specific objectives included:

- Evaluate the capabilities of ion selective membranes for soil nitrate and potassium sensing with respect to their sensitivity, lower detection limits, and selectivity against interferences of other ions.
- Investigate the effect of soil extracting solution on the response characteristics of ion selective membranes to predict nitrate and potassium concentrations in the solution.
- Determine a combination of ion selective membranes that is suitable for use with a real-time ISFET sensor for sensing nitrate and potassium ions in soil.

Materials and Methods

Reagents and Solutions

For the determination of nitrate concentration, quaternary ammonium compounds were used as ligands in non-porous PVC –based nitrate-selective membranes. The ligands – tetradodecylammonium nitrate (TDDA) and methyltridodecylammonium chloride (MTDA); and the plasticizers – nitrophenyl octyl ether (NPOE) and tri-(2-ethylhexyl) trimellitate (TOTM) were selected for testing based on previous studies (Nielson et al., 1976; Tsukada et al., 1989; Birrell and Hummel, 2000).

To prepare candidate potassium-selective membranes, according to the method reported previously (Knoll et al., 1994; Moody et al., 1988; Bae and Cho, 2002), valinomycin (potassium ionophore □) as a ligand, the NPOE, bis(2-ethylhexyl) sebacate (DOS), and bis(2-ethylhexyl) adipate (DOA) as plasticizers, and potassium tetrakis (4-chlorophenyl) borate (KTpClPB) as a lipophilic additive that reduces interferences by lipophilic anions in the analyte (Ammann, 1986) were purchased from Fluka (Ronkonkoma, N.Y.). All other chemicals used were of analytical reagent grade.

Extracting solutions were selected for calibrating the response characteristics of the nitrate and potassium ion-selective membranes. For the nitrate membranes, deionized (DI) water, 0.01M $CuSO_4$, and Kelowna were selected as base solutions; for the potassium membranes, DI water, Bray P_1, Mehlich III, and Kelowna solutions were selected. The solutions were prepared according to standard laboratory procedures (Missouri Agricultural Experimental Station, 1998), using double distilled water (18.1 MΩ cm^{-1}).

Preparation of Ion Selective Membranes and Electrodes

Two chemical compositions for nitrate and potassium membranes were used according to the procedures described in previous studies (Birrell and Hummel, 2000; Knoll et al., 1994, for nitrate and potassium, respectively). The nitrate ion-selective membranes were prepared with a mixture of 30 mg (15% wt) of ligand (TDDA or MTDA), 80 mg (40% wt) of plasticizer (NPOE or TOTM) and 90 mg (45% wt) of high-molecular-weight polyvinyl chloride (PVC). The composition of the potassium ion-selective membrane prepared was 4 mg (1% wt) of ligand (valinomycin), 1 mg (0.5% wt) of lipophilic additive (KTpClPB), 129.4 mg (64.70% wt) of plasticizer (DOS, NPOE, or DOA), and 65.6 mg (32.80% wt) of PVC.

The membranes were produced by dissolving the mixture in 2 ml of tetrahydrofuran (THF). The mixture was stirred until the membrane components were completely dissolved, poured into a 23-mm glass ring resting on a polished glass plate, and allowed to evaporate for 24 h at room temperature. The membrane, formed as a film, was removed from the glass plate, and three disks with a diameter of 2.5 mm were cut from each master membrane. The membrane disks were attached to the ends of PVC Hitachi ISE electrode bodies using the THF solvent. Prior to testing, the ion selective electrodes (ISEs) with the nitrate and potassium membranes were conditioned in 0.01M $NaNO_3$ and 0.01M KCl solution, respectively, for at least 6 h, so that steady electrical potentials could be obtained.

Each nitrate ISE electrode was filled with an internal solution consisting of 0.01M $NaNO_3$ and 0.01M NaCl. Potassium chloride (0.01M) was employed as the internal reference solution of the potassium electrodes. An Ag/AgCl electrode was immersed as the inner reference electrode. A double junction Ag/AgCl electrode (Omega Model PHE 3211) was used as the reference electrode. To dissuade contamination of sample analyte ions such as K^+ and NO_3^- from the reference electrode, 1M LiOAc was used as the outer reference solution in the reference electrode.

EMF Measurements

An automated test apparatus was designed for the simultaneous measurement of the electromotive forces (EMFs) of 16 ISE electrodes (Fig. 1) generated by the change in membrane potential at different ionic concentrations. To control the system and record values obtained from the ISE electrodes, a program was developed with Microsoft Access and Visual Basic. A Daqbook 200 portable PC-based data acquisition system and a 400-MHz Pentium computer were used to collect and store ISE electrode voltage outputs. Eight different solutions, contained in Teflon-coated buckets, were controlled by a multi-channel peristaltic pump and eight solenoid valves. The program automatically activated valves to control injection of solutions into the test stand, and controlled the speed of a pan motor to stir the test solutions (slow speed) during data collection, or to expel solutions from the sample solution holder (high speed) between tests.

To minimize current leakage and capacitive loading, and to reduce signal noise, the electrode outputs were conditioned using a 16-channel buffering circuit module equipped with operational amplifiers LF 356 N (input impedance, $10^{12}\ \Omega$/pF; bias current, < 8 nA), as shown in Fig 1. Control parameters were set to rinse the sample solution holder three times at each solution exchange to completely remove the residues of previous solutions. The EMF measurements were made with 15 s and 60 s for pre-measurement and measurement timing, respectively, after the injection of solution stopped during the cycle to observe if changes in EMF occurred during the measuring time of 1 min. The solutions were stirred throughout the measurement to obtain equilibrium potentials. Three measurements taken every 3 s were averaged and recorded for each standard solution in the testing sequence. Each test included three iterations of the complete testing sequence.

Sensitivity Test

For the nitrate sensing, two different sets of membrane combinations were prepared. The initial set included two TDDA-NPOE (A, B) membranes, two MTDA-NPOE (A, B) membranes, and

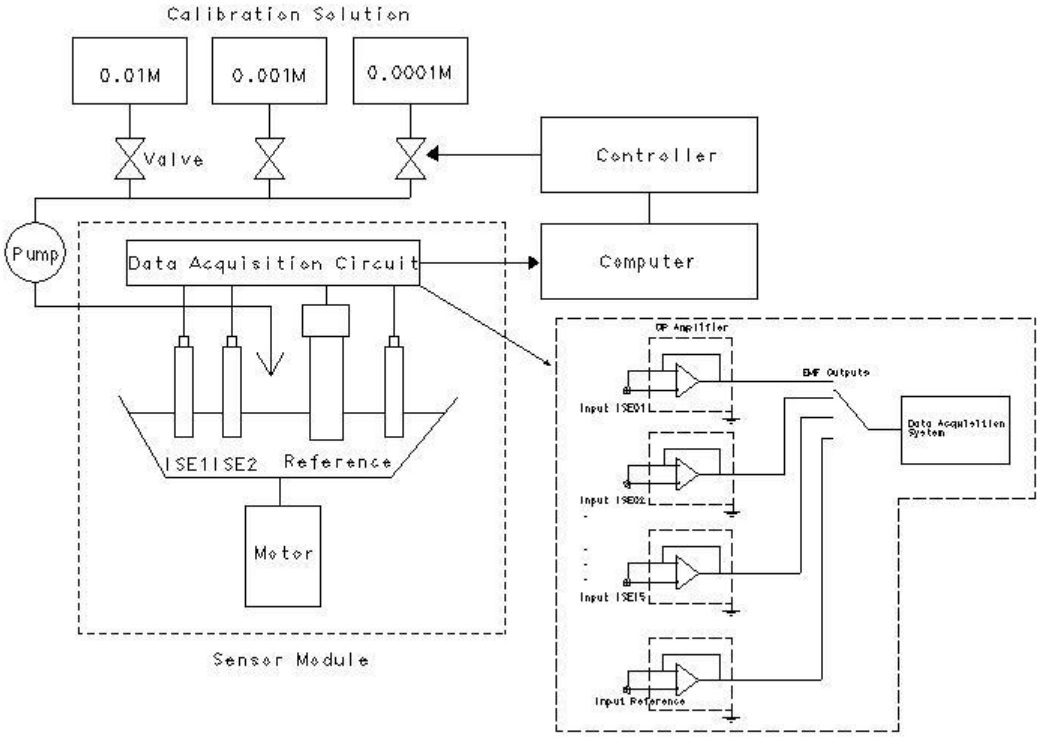

Figure 1. Schematic representation of ion selective electrode test apparatus.

one MTDA-TOTM (A) membrane. For the second test set, two TDDA-NPOE (A, B) membranes, one MTDA-NPOE (B) membrane, and two MTDA-TOTM (A, B) membranes were selected. For the sensitivity tests using potassium membranes, three different potassium membranes, Valinomycin-DOS, Valinomycin-NPOE, and Valinomycin-DOA and two nitrate membranes, TDDA-NPOE and MTDA-NPOE were tested. For the determination of membrane uniformity, three cuts from each master membrane were prepared, thereby resulting in a test setup containing 15 ISEs fabricated with five different membranes. The nitrate membranes were included in the potassium sensitivity test to investigate whether their response would be affected by the presence of other cations and anions. The tests of nitrate and potassium sensitivity, as described above, were conducted with three different solutions (DI, 0.01M CuSO4, and Kelowna) and four different soil extractants (DI, Bray P_1, Mehlich III, and Kelowna), respectively.

Six standard solutions having different concentrations of nitrate and potassium (10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1}mole/L) were prepared using $NaNO_3$ and KCl.

The effects of membrane composition and soil extracting solution on sensitivity were investigated by comparing the Nernstian slopes obtained from the linear relationship between the logarithm of the ionic activities of nitrate and potassium and EMFs of corresponding ISEs.

The Nernst equation was used to calculate the sensitivity:

$$EMF = E_o + E_J + S \log a_i \qquad (1)$$

where

EMF = electromotive force
E_o = standard potential
E_J = liquid-junction potential
S = Nerstian Slope (59.16 mv/Z_i for H_2O at 25 ^oC)
a_i = activity of single ion

The concentration can be converted to activities using single-ion activity coefficients in equation (2):

$$a_i = \gamma_i c_i \tag{2}$$

where a_i = single-ion activity (M)

γ_i = single-ion activity coefficient

c_i = ion molar concentration (M)

The single-ion coefficients are determined from the mean activity coefficients of the electrolyte, which are estimated using the Debye-Huckel formula (Morf, 1981). The Debye-Huckel equation is given as follows:

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1+Ba\sqrt{I}} \tag{3}$$

where A and B are constants with values of $0.51(10^9)$ and $3.3(10^9)$, respectively, at 25 ^oC, a is the ion size parameter, and Z is the charge on the ion. The ionic strength, I, is a measure of the total ions in solution, weighted according to their charges and concentrations, as in the following equation:

$$I = \frac{1}{2}\sum c_{i,j} z_{ij}^2 \tag{4}$$

Liquid-junction potentials are always generated when electrolytic solutions of different ionic compositions are in contact (Ammann, 1986). A typical reference electrode has a liquid-junction potential at the junction of the reference electrode with the sample solution. For this experiment, the potential was assumed to be constant.

Selectivity Test

The Nernst equation used in the sensitivity test assumes that the membrane is ideally specific to a certain ion. However, in most cases the membrane responds to other interfering ions and the measured EMF is the sum of the membrane potentials. The extent of interference is expressed in the Nikolski-Eiseman equation (Eqn. 5) in terms of the electrode potential and a selectivity coefficient as follows:

$$EMF = E_o + E_J + S\log\left[a_i + \sum K_{ij}(a_j)^{Z_i/Z_j}\right] \tag{5}$$

where

E_o = standard potential

E_J = liquid-junction potential
S = Nernstian Slope (theoretically, 59.16 mv/Z_i for H_2O at 25 ^oC)
a_i = activity of primary ion
a_j = activity of interference ion
Z_i = charge of primary ion
Z_j = charge of interference ion
K_{ij} = selectivity coefficients

The selectivity factor, K_{ij}, is a measure of the preference by the sensor for the interfering ion J relative to the ion I to be detected (Ammann, 1986). Obviously, for ideally selective membranes all of the K_{ij} values should be zero. A selectivity factor <1 indicates a preference for the primary ion *i*, relative to the interference ion *j*. Selectivity factors are determined experimentally using several techniques: the separate solution method (SSM), the fixed interference method (FIM), and the fixed primary ion method (FPM) (IUPAC, 1994).
In this test, the selectivity factors were determined using the separate solution method (SSM) in which the corresponding selectivity factors are calculated based on EMF values obtained with pure single electrolyte solutions of the primary ion (0.01M) and interference ion (0.1 M) in the following way:

$$K_{i,j} = 10^{\frac{E_J - E_i}{S}} \frac{a_i}{a_j^{Z_i / Z_j}} \qquad (6)$$

where, a_i = activity of 0.01M primary ion
a_j= activity of 0.1M interfering ion
E_i = EMF measured with solution of 0.01M primary ion
E_j = EMF measured with solution of 0.1M interfering ion
S = Nernstian Slope obtained with 0.01M and 0.1M primary ion solutions
The selectivity tests were conducted with the same sets of membranes as those used in the sensitivity tests. The selectivity of each membrane in different base solutions for nitrate and potassium over interference ions was investigated in the following order: bicarbonate ($NaHCO_3$), chloride (NaCl), and bromide (NaBr) for nitrate membrane selectivity; and magnesium ($Mg(NO_3)_2$), calcium ($Ca(NO_3)_2$, sodium ($NaNO_3$), lithium ($LiNO_3$), aluminum ($Al(NO_3)_3$), and ammonium (NH_4NO_3) for potassium membrane selectivity using sodium salts and nitrate salts, respectively.
During the selectivity test sequence, the EMFs in 0.1M and 0.01M primary ion solutions were continuously monitored before the EMFs were measured with solutions of 0.01M primary ion and 0.1M interference ions to obtain precise data for Nernstian slope calculations for determining corresponding selectivity factors for each interference ion. The SAS General Linear Model Procedure (GLM) was used to determine whether the selectivity factors of the membranes in the presence of different extracting solutions were significantly different, using Duncans Multiple-Range Test at a significance level of 5%.

Results and Discussion

Evaluation of Nitrate Ion-Selective Membranes

The response of the nitrate ion-selective electrodes having three different membranes (TDDA-NPOE, MTDA-NPOE, and MTDA-NPOE) are shown in DI water (Fig. 2a) and in the 0.01M $CuSO_4$ (Fig. 2b) solution, when nitrate concentrations ranged from 10^{-6} mole/L to 10^{-1} mole/L. Each curve was obtained by averaging the EMF values measured with six individual electrodes of each membrane type (A and B). All membrane potentials were normalized by setting the EMF values measured in 0.1mole/L nitrate solution to be 50 mV.

As shown in Fig. 2a, in the DI extractant, the EMF values generated from all of the tested membranes were linearly proportional to the logarithm of the nitrate concentration (ionic activity) in the range $10^{-1} \sim 10^{-5}$ mole/L. However, there appeared to be little change in voltage readings in the range of $10^{-6} \sim 10^{-5}$ mole/L nitrate concentrations. All of the electrodes exhibited a linear

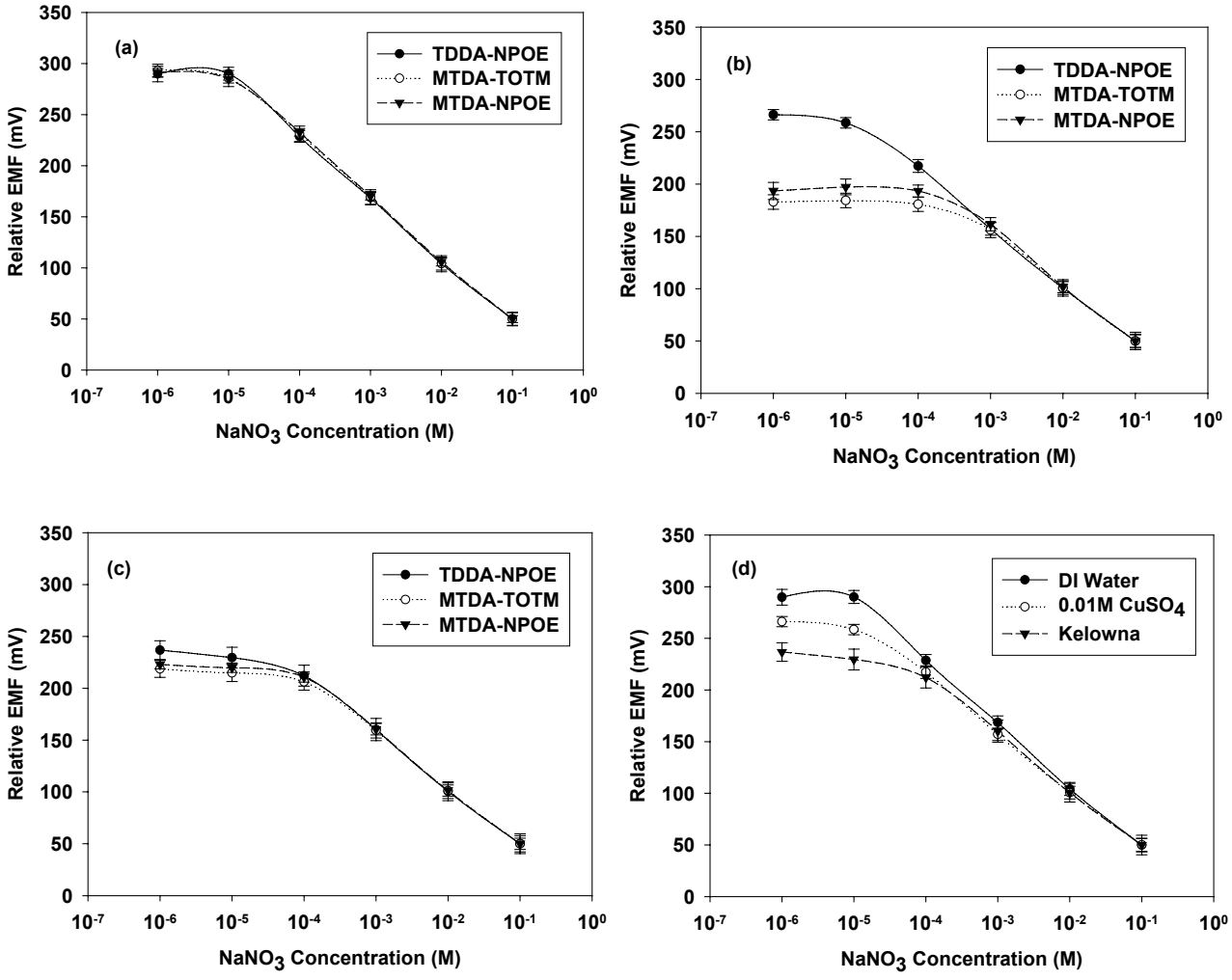

Figure 2. Electrode voltage potential vs. nitrate concentration for different nitrate membranes: (a) in DI water, (b) in 0.01M $CuSO_4$, (c) Kelowna solution, and (d) effect of

extractant on membrane sensitivity for the TDDA-NPOE nitrate membrane.

response over a range of 10^{-5} mole/L to 10^{-1}mole/L nitrate concentrations and their lower detection limits, calculated by the IUPAC method, were determined to be $9.2x10^{-6} \sim 1.1x10^{-5}$mole/L. There was no difference in sensitivity between individual membranes when the DI water was used as the extracting solution.

When the electrodes were measured in 0.01M $CuSO_4$ solution (Fig. 2b), a decrease in sensitivity occurred at nitrate concentrations less than 10^{-4} mole/L across all membranes. However, the TDDA membranes showed higher sensitivity at low concentrations than did the MTDA membranes. The linear response range of the TDDA-NPOE membrane seemed to be $\sim10^{-5}$ $\sim10^{-1}$ mole/L, whereas the linear range of the MTDA membranes existed in the range of 10^{-4} $\sim10^{-1}$ mole/L nitrate concentration.

When evaluating nitrate sensitivity in the Kelowna solution (Fig. 2c), the response of the nitrate membranes to change in the nitrate concentration was decreased considerably as compared to the DI water and 0.01M CuSO4 solutions. The EMFs obtained with the nitrate membranes when using the Kelowna solution were considerably decreased at low concentrations ($<10^{-4}$ mole/L), thereby resulting in the lower detection limit of $3.7 \sim 6.2x10^{-5}$ mole/L nitrate concentration. The results suggest that two anions such as acetate (CH_3COO^-) and fluoride (F^-) present at the Kelowna solution might have an effect on the sensitivity of the three nitrate membranes.

A comparison of the sensitivity results for one membrane across the DI, 0.01M $CuSO_4$, and Kelowna extractants (Fig. 2d) indicates that the sensitivities of nitrate membranes at low nitrate concentrations ($<10^{-4}$ mole/L) are affected by the extracting solutions. The usable portion of the nitrate concentration: EMF curve appears to be from 10^{-1} to10^{-5} mole NO_3/L, which encompasses the range of interest ($7.1x10^{-5} \sim 2.1x10^{-4}$ mole NO_3/L) for soil nitrate sensing.

SAS GLM comparisons of the sensitivities of the nitrate membranes for different nitrate concentration ranges in the presence of each extracting solution (Table 1) show that the sensitivity of the membranes varied considerably among the different base solutions. The sensitivities of the membranes at low nitrate concentrations, when using either the 0.01M $CuSO_4$ or Kelowna solutions, significantly reduced the sensitivity slopes when data from the full range of concentrations was included in the calculations. In general, the membrane sensitivities obtained with the DI extractant were higher than those measured with the $CuSO_4$ and Kelowna solutions. In the range of 10^{-4} to 10^{-1} mole/L nitrate concentrations, the averaged sensitivity slopes were -62 ~ -63 mV/decade for DI water, -53 ~ -54 mV/decade for Kelowna solution, and -45 ~ -56 mV mV/decade for the 0.01M $CuSO_4$ solution.

According to Duncans Multiple-Range test, in the 0.01M $CuSO_4$ solution, when the EMF values obtained in 10^{-5} mole/L and 10^{-4} mole/L nitrate solutions were included, the sensitivities of the TDDA-NPOE membranes were higher than those of the MTDA-NPOE and MTDA-TOTM membranes. However, in the Kelowna solution, in the range of 10^{-4} mole/L to 10^{-1} mole/L nitrate concentrations, there was no significant difference between TDDA-NPOE and MTDA-NPOE membranes in terms of response slope.

Potentiometric selectivity coefficients, obtained by the separate solution method, with respect to the interference anions, bicarbonate (HCO_3), chloride (Cl), and bromide (Br) in different extracting solutions are summarized in Table 2. In the tests using the $CuSO_4$ solution, results for the bicarbonate ion were not obtained because the bicarbonate chemical was not completely dissolved and formed a precipitate in 0.01M $CuSO_4$ solution.

Table 1. Comparison of sensitivity slopes of nitrate membranes by extractant type.

Membrane Composition	Concentration Range 10^{-1}M to 10^{-5}M	10^{-1}M to 10^{-4}M	10^{-1}M to 10^{-3}M
	------ *sensitivity (mV/decade)* ------		
DI Water			
MTDA-TOTM	-61.27a*	-63.00a	-62.54a
MTDA-NPOE	-61.40a	-63.71b	-63.52b
TDDA-NPOE	-62.23b	-62.44c	-62.68a
Kelowna Solution			
MTDA-TOTM	-43.63a	-53.01a	-55.24a
MTDA-NPOE	-45.06b	-54.48b	-55.70a
TDDA-NPOE	-47.17c	-54.92b	-55.83a
0.01M $CuSO_4$ Solution			
MTDA-TOTM	-35.17a	-45.46a	-54.57a
MTDA-NPOE	-39.00b	-49.78b	-55.03a
TDDA-NPOE	-54.00c	-56.80c	-57.36b

* Membrane sensitivities within a nitrate concentration and within an extracting solution comparison with the same letter are not significantly different at the 5% level, based on Duncans Multiple-Range Test.

The results obtained from the SAS GLM analysis showed that the selectivity responses of the membranes were affected considerably by both membrane type and extracting solution type. The TDDA membranes displayed greater selectivity for nitrate against the interfering species than did the MTDA membranes. Also, the highest selectivity of the tested interference ions for nitrate over the anions, chloride and bromide, was obtained when using the 0.01M $CuSO_4$ extracting solution. Bromide was included in the selectivity tests as a check ion, since the literature shows little or no selectivity for nitrate over bromide. The selectivity of the membranes for nitrate over bromide was lowest (largest selectivity factor (log K_{ij})), and approximately one for all membranes and extracting solutions.

Evaluation of Potassium Ion-Selective Membranes

The responses of three valinomycin membranes with different plasticizers (DOS, NPOE, and DOA) to varying potassium concentration were evaluated (Fig. 3) when four different soil extractants (DI water, Kelowna, Bray P_1, and Mehlich III) were used as base solutions. In general, as found in the nitrate membrane test, the EMF values obtained with tested potassium membranes were linearly proportional to changes in potassium concentration ranging from 10^{-3} mole/L to 10^{-1} mole/L regardless of the tested soil extracting solution.

Table 2. Comparison of selectivity coefficients of nitrate membranes by extractant type.

Membrane Composition	Ionic Species		
	HCO3	Cl	Br
	------ *selectivity factor (log K)* ------		
DI Water			
MTDA-TOTM	-2.42a*	-1.67a	-0.62a
MTDA-NPOE	-2.62b	-1.77b	-0.66b
TDDA-NPOE	-3.47c	-2.30c	-0.92c
Kelowna Solution			
MTDA-TOTM	-2.73a	-1.72a	-0.73a
MTDA-NPOE	-2.89b	-1.81b	-0.77b
TDDA-NPOE	-3.22c	-2.07c	-1.03c
0.01M CuSO4 Solution			
MTDA-TOTM	-	-2.02a	-0.79a
MTDA-NPOE	-	-2.13b	-0.86b
TDDA-NPOE	-	-2.78c	-1.15c

* Membrane sensitivities within a nitrate concentration and within an extracting solution comparison with the same letter are not significantly different at the 5% level, based on Duncans Multiple-Range Test.

All of the tested potassium membranes in the DI water (Fig. 3a) showed a linear Nerstian response with typical slopes of 54.6 ~ 58.2 mV per decade change in activity of potassium ion when the KCl concentrations were above 10^{-5} mole/L. As potassium concentration was decreased to 10^{-6} mole/L, the response slope was reduced but some response to potassium ion concentration was still exhibited. Therefore, it was expected that the lower detection limits of the tested potassium membranes in DI water might be below 10^{-6}M. Such results are comparable to those measured with standard PVC potassium membranes described by Oh et al. (1998).

When the responses of the potassium membranes to different potassium concentrations in the Kelowna and Bray P_1 solutions were measured (Fig. 3b and c, respectively), at low potassium concentrations (<10^{-4} mole/L), the response slopes were reduced compared to those measured in the DI water (Fig. 3a). There was little response of any of the three membranes in the potassium concentration range of 10^{-6}mole/L to 10^{-4}mole/L. Based on the regression analysis using the EMF values in the range of 10^{-1} to 10^{-3} mole/L, the lower detection limits for potassium were 1.7~2.7x10^{-4} mole/L and 2.6~3.1x10^{-4} mole/L in the Kelowna and Bray P_1 solutions, respectively.

The response ranges of three potassium membranes in the Mehlich III solution (Fig. 3d) were considerably reduced as compared to the other extracting solutions, thereby resulting in decrease in sensitivity (< 40 mV/decade) at higher potassium concentrations (10^{-3} ~10^{-1} mole/L). In addition, the lower detection limit for potassium was much higher (10^{-3}mole/L) than for the other solutions, since the EMFs measured with the potassium-selective electrodes were almost identical in the potassium concentration range of 10^{-6} to 10^{-3}mole/L. This poor detection limit is related to the fact that the Mehlich III solution contains various cations such as $NH4^+$and H^+ that interfere with potassium measurement.

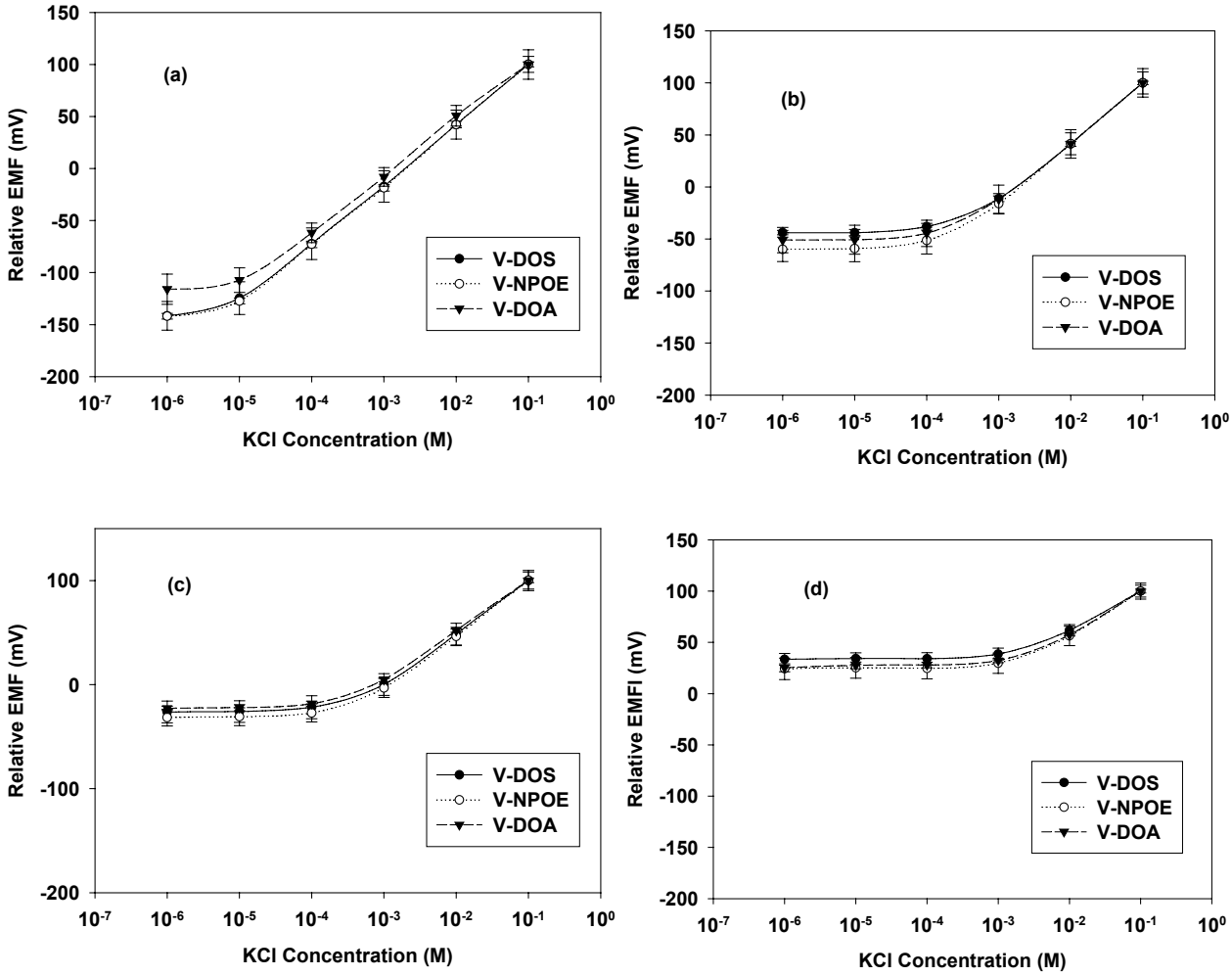

Figure 3. Electrode voltage potential vs. potassium concentration for potassium membranes: (a) in DI water, (b) in Kelowna solution, (c) in Bray P_1 solution, and (d) in Mehlich III solution.

Using the response data for the potassium membranes that contain DOS as the plasticizer, the effect of different base solutions on sensitivity response of potassium membranes can be illustrated (Fig. 4). As shown in the figure, the lower detection limits and response slopes for potassium were significantly affected by soil extractant. These results indicate that the responses of potassium-selective membranes are quite sensitive to the presence of other cations and anions contained in the soil extracting solutions, thereby resulting in significant differences in the membrane potentials upon varying potassium concentrations. However, even though the membrane sensitivity is reduced when using the Kelowna solution as compared to DI water, the usable range of the KCl concentration:EMF relationship (10^{-1} to ~10^{-4}) still encompasses the range of interest for soil potassium sensing (10^{-3} to 10^{-4}).

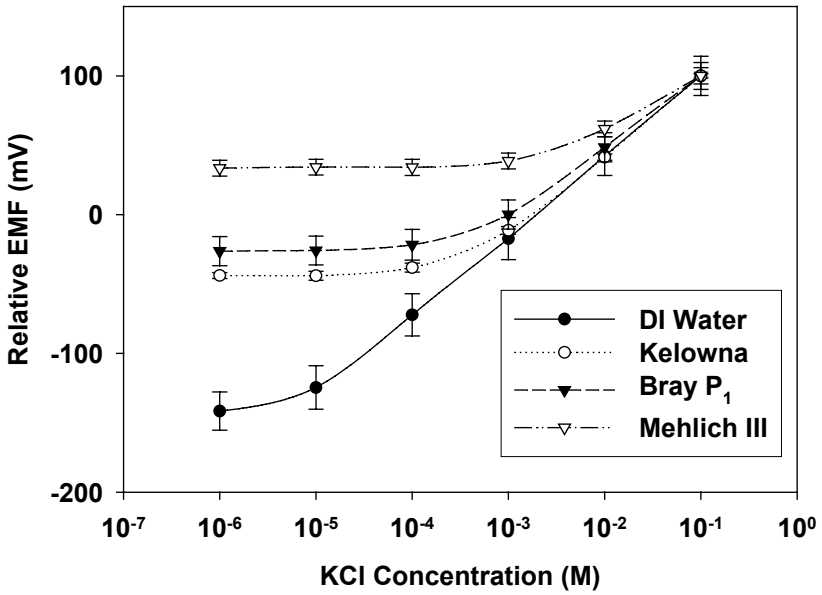

Figure 4. Effect of soil extractant on sensitivity responses of potassium membranes.

Fig. 5 shows the effect of different base solutions on sensitivity response of nitrate selective membranes with TDDA and NPOE as ligand and plasticizer, respectively. When nitrate-selective electrodes containing TDDA-NPOE and MTDA-NPOE (data not shown, but similar pattern obtained) were measured in the DI water extractant, the nitrate membranes were significantly affected by the amount of chloride ion present, showing almost Nerstian slopes (59

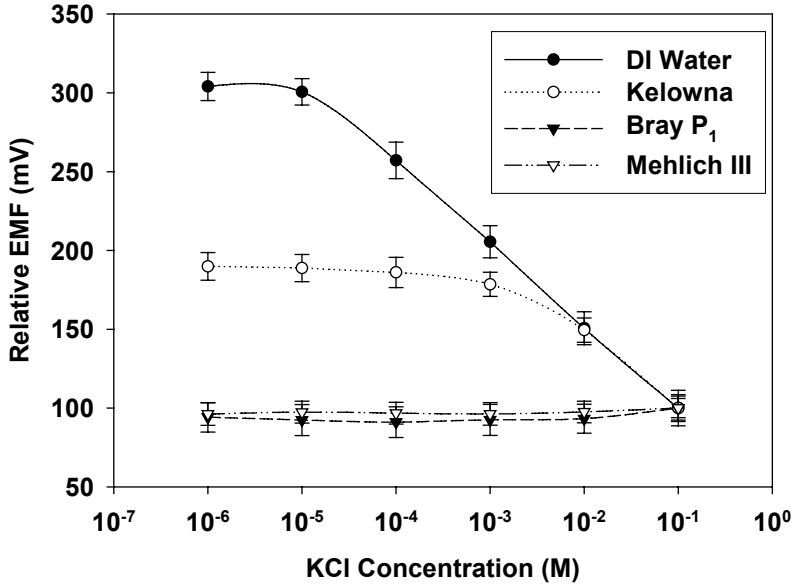

Figure 5. Effect of soil extractant on sensitivity responses of nitrate membranes.

mV/decade). In contrast, in the other solutions, at potassium chloride concentrations ranging from 10^{-6} to 10^{-3} mole/L, the EMF values measured with the nitrate selective membranes were almost constant, regardless of the potassium and chloride concentrations. Although the tested

nitrate-selective electrodes were sensitive to the chloride ion in DI water, they would also show good sensitivity for nitrate, if a small amount of nitrate were added to the DI water because the tested nitrate-selective membranes are 62~200 times more sensitive to nitrate than to chloride, based on the results of the selectivity test for the nitrate membranes (Table 2).

Table 3 shows the comparison of membrane sensitivity for different potassium concentrations in the presence of each extracting solution. The effect of extracting solution on sensitivity of the three potassium membrane was apparent, and plasticizer type affected the response slopes of mV/decade). In general, the NPOE-based membrane responded most rapidly to changes in potassium concentration.

Table 3. Comparison of sensitivity slopes of potassium membranes by extractant type.

	Concentration Range		
Membrane Composition	10^{-1}M to 10^{-5}M	10^{-1}M to 10^{-4}M	10^{-1}M to 10^{-3}M
	------ *sensitivity (mV/decade)* ------		
DI Water			
V-DOS	57.96a*	59.87a	61.94a
V-NPOE	58.59a	60.21a	62.65a
V-DOA	54.20b	56.57b	57.12b
Kelowna Solution			
V-DOS	36.87a	46.97a	56.20a
V-NPOE	41.30b	51.50b	58.63b
V-DOA	38.87c	48.96c	56.50a
Bray P_1 Solution			
V-DOS	32.47a	41.95a	51.16a
V-NPOE	33.81b	43.73b	52.89b
V-DOA	31.73c	40.79c	48.73c
Mehlich III Solution			
V-DOS	15.96a	22.15a	30.86a
V-NPOE	18.16b	25.36b	35.39b
V-DOA	17.46b	24.20b	34.06b

* Membrane sensitivities within a nitrate concentration and within an extracting solution comparison with the same letter are not significantly different at the 5% level, based on Duncans Multiple-Range Test.

When the three potassium membranes were tested in solutions containing 0.1M and 0.01M KNO_3 or KCl solutions (Table 4), the NPOE-based membranes gave unacceptable response slopes (< 7 mv/decade) in the presence of NO_3 of 0.1M concentration. Thus, high (0.1M) nitrate concentration interfered with the NPOE-based potassium membrane tested in all of the solutions. These results are identical to those obtained by Cuin et al. (1999), who reported that the presence of high concentrations of nitrate (0.2M) affected the response of a K^+ sensor fabricated with a valinomycin membrane containing NPOE as the plasticizer. These tests show that the DOS- and DOA-based membranes exhibit much less nitrate interference as compared with the NPOE-based membranes.

Table 4. The effect of nitrate on the response of potassium membranes.

	Plasticizer					
	DOS		NPOE		DOA	
Extractant	KCl	KNO_3	KCl	KNO_3	KCl	KNO_3
	------- *sensitivity (mV/decade)* -------					
DI Water	62.6	58.6	62.6	-4.3	53.4	57.5
Kelowna Solution	59.8	54.7	59.7	-6.9	59.8	54.1
Bray P_1 Solution	53.6	55.6	55.8	0.67	50.1	53.7
Mehlich III Solution	38.7	47.5	44.2	3.9	43.1	45.5

A comparison of the mean selectivity coefficients (log K) of the DOS- and DOA-based potassium membranes, obtained by the separate solution method, for the six cations in the four different solutions is shown in Table 5. In the tests using the NPOE-based potassium membranes, the responses for each interference ion were comparable to those obtained by the DOS and DOA-based membranes (data not shown). However, because the sensitivities of the NPOE-based membranes were affected by nitrate concentrations between 0.1M and 0.01M, significantly different selectivity coefficient values resulted for this membrane.

The results obtained from the SAS multiple comparison analysis indicated that membrane selectivity was affected by plasticizer type (Table 5), and selectivity for potassium over other cations was enhanced when the DOA-based membrane was used. However, both membranes based on the valinomycin showed the same order in selectivity magnitude: $NH_4^+ << Na^+ \sim Li^+ < Mg^{2+} \sim Ca^{2+} \sim Al^{3+}$. In general, the selectivity coefficients for potassium over most of the tested cations (except NH_4^+) were high enough to obviously detect potassium in the tested extracting solutions (except Mehlich III), which is consistent with the results reported by other researchers (Knoll et al., 1994; Bae and Cho, 2002; Oh et al., 1998).

Using only the data for the DOS-based potassium membrane (Fig. 6), the effect of base solution on membrane selectivity is illustrated. Obviously, the selectivity for potassium over the tested interfering cations was affected by soil extractant. However, the selectivity of potassium in the presence of ammonium was nearly constant regardless of base solution type with logarithmic selectivity coefficients (log K) of -1.42 ~ -1.82. In the DI water, the highest selectivity towards potassium was observed. As poor sensitivity for potassium was observed in the Mehlich III solution, the selectivity performance for potassium over other cations was decreased. This phenomenon is probably due to kinetic limitations in the transfer of potassium ions by various other cations and anions present in the Mehlich III solution (Eugster et al., 1991; Oh et al., 1998).

Table 5. Comparison of selectivity coefficients of potassium membranes by extractant type.

Membrane Composition*	Interference Ion					
	Al(+3)	Mg(+2)	Ca(+2)	Li(+1)	Na(+1)	NH_4(+1)
	------ *selectivity factor (log K)* ------					
DI Water						
V-DOS	-4.05a**	-3.98a	-4.00a	-3.60a	-3.54a	-1.64a
V-DOA	-4.45b	-4.40b	-4.41b	-3.87b	-3.95b	-1.77b
Kelowna Solution						
V-DOS	-2.93a	-2.94a	-2.88a	-2.61a	-2.57a	-1.63a
V-DOA	-3.12b	-3.13b	-3.07b	-2.79b	-2.75b	-1.82b
Bray P_1 Solution						
V-DOS	-2.55a	-2.53a	-2.54a	-2.18a	-2.19a	-1.69a
V-DOA	-2.76b	-2.71b	-2.72b	-2.34b	-2.39b	-1.79b
Mehlich III Solution						
V-DOS	-1.99a	-1.97a	-1.90a	-1.62a	-1.57a	-1.42a
V-DOA	-2.13b	-2.06b	-1.89a	-1.72b	-1.38a	-1.47a

*Selectivity coefficients were not calculated for the V-NPOE membrane, since the sensitivities of the membrane were affected by nitrate concentration (Table 4)

** Membrane sensitivities within a nitrate concentration and within an extracting solution comparison with the same letter are not significantly different at the 5% level, based on Duncans Multiple-Range Test.

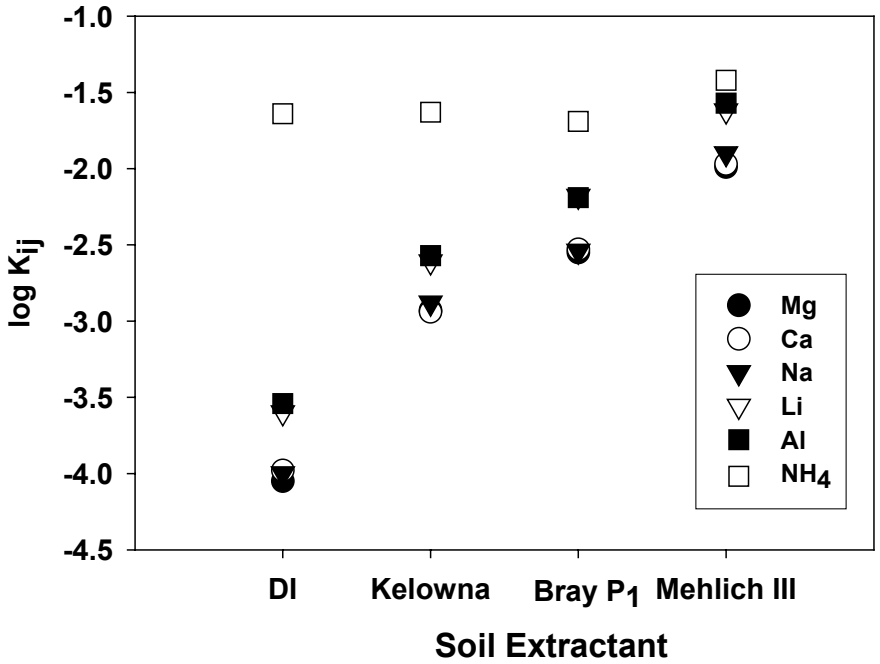

Figure 6. Effect of soil extractant on selectivity response of the valinomycin-DOS membrane.

Conclusions

To select ion-selective membranes suitable for the measurement of nitrate and potassium ions in soil, six PVC polymer membranes doped with electroactive materials were prepared, and their response characteristics to electrolytes in various soil extractants were investigated.

All of the nitrate ion-selective membranes based on tetradodecylammonium nitrate (TDDA) or methlytridodecylammonium chloride (MTDA) exhibited a linear response to nitrates when nitrate concentrations were above 10^{-3} mole/L, irrespective of which soil extracting solution was used. However, at low nitrate concentrations, i.e., below 10^{-4} mole/L, the sensitivity responses of the membranes to nitrate were reduced when 0.01M $CuSO_4$ and Kelowna extracting solutions were used as base solutions, as compared to that obtained in DI water, thereby resulting in increase in the lower detection limits. These results indicate that the interfering ions present in soil extractants may have an effect on the sensing response of the nitrate membranes. The highest selectivity of the membranes for nitrate over interference ions was found when using the 0.01M $CuSO_4$ solution. The selectivity performance of the tested nitrate membranes appeared to be satisfactory in measuring nitrates in the presence of chloride ions since the membranes showed 62~200 times more sensitive to nitrate than to chloride. The better selectivity of the nitrate membranes with respect to chloride is important in the selection of a membrane for sensing soil nitrate since chloride ions may be present in soils in concentrations similar to those of nitrates (Birrell and Hummel, 2000). In general, the TDDA-based membrane showed greater sensitivity and better selectivity for nitrate than did the MTDA-based membranes. The tested TDDA-NPOE membrane would be capable of detecting low concentrations of nitrate in soils (typically, 10~30 mg NO_3/kg soil is equal to $7.1x10^{-5} \sim 2.1x10^{-4}$ mole NO_3/L solution with a dilution ratio (solution: soil) of 10:1) based on the estimated lower detection limits of about $9.2x10^{-6} \sim 1.1x10^{-5}$ mole/L, $1.5\sim4.6x10^{-5}$ mole/L, and $3.7\sim6.2x10^{-5}$ mole/L in DI water, the 0.01M $CuSO_4$ solution and the Kelowna solution, respectively.

The sensitivity and selectivity responses of the tested valinomycin-based potassium membranes were obviously influenced by both plasticizer type and soil extractant type. The NPOE-based membranes generally showed greater sensitivity whereas the DOA-based membranes exhibited superior selectivity for potassium over the interfering anions used. Use of the valinomycin-based membranes in the Mehlich III solution, which is one of the most commonly used soil extractants, may be improper because the sensing responses of the membranes, obtained in the Mehlich III were considerably reduced as compared to those measured with other soil extractants, thereby leading to the insensitivity at typical potassium levels in soils of 50~150 mg K/kg soil, which correspond to $1.3x10^{-4} \sim 3.8x10^{-4}$ mole K/L. However, in the other extractants such as DI water, Kelowna solution, and the Bray P_1 solution, the responses of the valinomycin-based membranes to potassium were sensitive enough to determine the typical range of potassium concentrations in soil. Therefore, use of the tested valinomycin-based membranes on the tested soil extractants except Mehlich III would allow the determination of potassium levels in soils.

Acknowledgments

The authors appreciate the assistance of the following USDA-ARS Cropping Systems & Water Quality Research Unit employees: Scott T. Drummond -- for contributions to the development of the computer interface and control software, and Joel D. Haden and Robert L. Mahurin -- for their assistance in fabrication of the test stand.

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